Separation of Heavy-Metal Ions from their Water Solutions by Xonotlite Crystal Compacts

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Compacts of Xonotlite crystal powders fired to temperatures ranging from 200° to 1000°C showed a great ability in separating heavy-metal ions from their water solutions and also fairly high compressive strengths even in the solutions. A mechanism of the separation of heavy-metal ions by the Xonotlite crystal compacts was investigated, especially in copper sulphate solutions. When the Xonotlite crystal compacts is immersed in the copper sulphate solution, Ca^{2+} ions in the Xonotlite crystals dissolve into the solution. Increase in the pH of the solution causes the Cu^{2+} ions to precipitate as $Cu_4(SO_4)(OH)_6$ crystals on the surface of the fibrous crystals intercrossing each other in the compact.

I INTRODUCTION

Hydrated calcium silicates prepared by hydrothermal syntheses, especially, Xonotlite, $Ca_6Si_6O_{17}(OH)_2$, and Tobermorite, $Ca_5(Si_6O_{18}H_2)\cdot 4H_2O$ show excellent abilities in separating heavy-metal ions from their water solutions. The present authors have found that of these two crystals Xonotlite crystals are most suitable for industrial uses to separate heavy-metal ions from their water solutions, since their compacts, after fired to temperatures ranging from 200° to 1000°C, keep their shape for a long time even in the water solutions. In a present paper, the ability of Xonotlite compacts in separating heavy-metal ions from their water solutions as well as the mechanism of separation of heavy-metal ions are presented. Xonotlite compacts have been used widely as the light heat-insulating materials since their structure is thermally stable and porous.[1] On preparation of Xonotlite by hydrothermal synthesis there are a number of reports.[2]

II EXPERIMENTAL

II. 1 Preparation of Samples

Xonotlite crystals prepared by Japan Metals and Chemicals Co., Ltd. were used as the starting materials. The method for their preparation was to autoclave a suspension of freshly slaked $Ca(OH)_2$ and finely amorphous silica powders in water to a total solids ratio of 10 at 190°C for 6 hours. The silica powders were a by-product in manufacturing ferrosilicon alloys. The CaO/SiO_2 ratio in the suspension was 1.0 by mole. The X-ray diffraction diagram and I. R. transmission curve of the synthesized Xonotlite are shown in Fig. 1 which are almost identical to those of natural Xonotlite crystals, respectively, described in references.[3,4]

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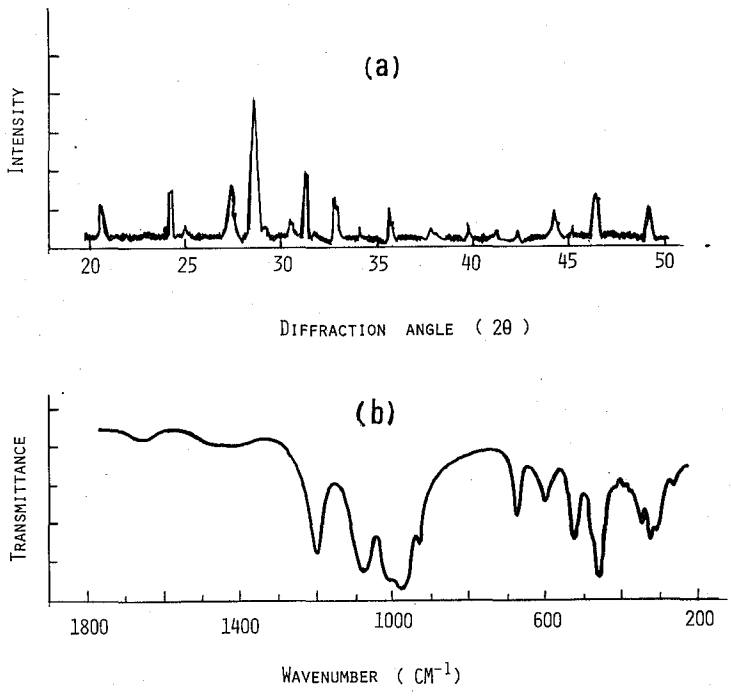

Fig. 1. X-ray diffraction pattern (a) and I. R. transmission curve (b) of Xonotlite crystal powders used in this experiment.

A wet mass of the synthesized Xonotlite crystals was formed with an extrusion method (forming pressure, about 5 Kg/cm^2) into two cylindrical forms, the one 3 mm in diameter and 4 mm in height and the other 20 mm in diameter and 15 mm in height, and fired at temperatures ranging from 200° to 1000°C for 30 minutes; the small ones were used to examine their ability in separating heavy-metal ions and the large ones to measure compressive strength in water.

II. 2 **Quantitative Analyses of Heavy-Metal Ions**

The small cylindrical pieces of Xonotlite compact were immersed in total amounts of 3.0 g in $CuSO_4 \cdot 5H_2O$ solutions containing 200, 2000 and 2500 ppm of Cu(II), respectively. After immersed at room temperature for various times, Xonotlite compacts were taken out from the solutions and the amounts of Cu^{2+} ions remaining in the solutions were determined by spectrophotometric analyses. The ability of the Xonotlite compact in separating heavymetal ions was also examined for $CdCl_2$, $Cr(NO_3)_3 \cdot 9H_2O$, $Pb(NO_3)_2$ and $HgCl_2$ solutions containing 200 ppm of each heavy-metal ion. The amounts of Cd^{2+}, Cr^{3+}, Pb^{2+} and Hg^{2+} ions in these solutions were measured also by the spectrophotometric method[5]. The Cd^{2+} and Hg^{2+} ions were extracted from their solutions into an organic solvent (carbontetrachloride) as dithizonates. As described later, when the Xonotlite compacts are immersed in the water solutions containing these heavy-metal ions, Ca^{2+} ions in the Xonotlite crystals dissolve into the solutions. The amounts of Ca^{2+} ions dissolved were determined by the Chelate titration. In some cases, this titration method was also applied to the measurement of the amounts of Cu^{2+} ions to confirm their values determined by the spectrophoto-

metric analyses.

II. 3 Measurements of Compressive Strengths of Xonotlite Compacts Immersed in Water

The Xonotlite crystal compact formed into a shape is more convenient for use as the adsorbent of heavy-metal ions than the powdered Xonotlite crystals, since it can be taken out easily from the heavy metal solutions and subjected to its regeneration process after its use. Conditions required for the compact is that it must keep its shape in the water solution for a long time, still keeping high its ability in separating heavy metal ions. Furthermore, when the compacts are used, they are ordinaly piled up in a tower through which the heavy metal solutions flow. Therefore, the compacts must have a strength sufficient enough to withstand a definite load in water.

In order to evaluate the degree of strength of the Xonotlite compacts in water, the large cylindrical specimens, previously fired at various temperatures for 30 minutes, were immersed in water for one hour and their compressive strengths, before and after the water immersion, were determined.

III RESULTS AND DISCUSSIONS

III. 1 Ability of Xonotlite Compacts in Separating Heavy-Metal Ions

Table I gives the results of the experiments in which the small cylindrical specimens, previously fired at various temperatures for 30 minutes, were immersed in total amounts of 3.0 g in 100 cc of the $CuSO_4 \cdot 5H_2O$ solution containing 200 ppm of Cu(II) for one hour. The results indicates that the decrease in Cu(II) concentration in the solution caused by immersion of the compacts is the largest for the compact fired at 600°C.

Table II shows the ability of the Xonotlite compacts, previously fired at 600°C for 30 minutes, in separating the other ions, Cd^{2+}, Cr^{3+}, Pb^{2+} and Hg^{2+} ions, from their solutions. The Xonotlite compacts were immersed in total amounts of 3.0 g in 100 cc of the solution containing 200 ppm of each ion. The results shows that the ability of the compacts in separating the above heavy-metal ions is also very high and its degree is much the same as that in Cu^{2+} ion (ref. Table I).

Table III gives comparison of the ability of Xonotlite powders (100 to 200 mesh) in separating Cu^{2+} ions from 100 cc of $CuSO_4 \cdot 5H_2O$ solution containing 2000 ppm of

Table I. Ability of Xonotlite Compacts Fired at Various Temperatures in Separating Cu^{2+}ions from $CuSO_4 \cdot 5H_2O$ Solutions.

Firing temperature (°C)	Cu(II) concentration in solution (ppm)		Percentage of Cu(II) removed (%)
	Before immersion of Xonotlite	After immersed for one hour	
200	200	42	78
400	200	15	92
600	200	6.0	97
800	200	9.9	95
1000*	200	38	78

* Xonotlite fully converted to β-Wollastonite above this temperature.

Table II. Ability of Xonotlite Compacts Fired at 600°C for 30 Minutes in Separating Heavy-metal ions from their Solutions.

Ion	Concentration of heavy-metal ions in solution (ppm)		Percentage of heavy-metal ions removed (%)
	Before immersion of Xonotlite	After immersed for one hour	
Cd(II) $CdCl_2$	200	1.0	99
Cr(III) $Cr(NO_3)_3 \cdot 9H_2O$	200	5.0	97
Pb(II) $Pb(NO_3)_2$	200	2.6	99
Hg(II) $HgCl_2$	200	9.0	95

Table III. Comparison of Xonotlite Powders with other Adsorbents in their Ability in Separating Cu^{2+} ions from $CuSO_4 \cdot 5H_2O$ Solutions.

Sample*	Amount of Cu(II) removed (m.eq/g)	Percentage of Cu(II) removed (%)**
Xonotlite (fired at 600°C)	6.88	100
Ca-charcoal	2.25	37
Na-charcoal	2.61	42
Active carbon	0.36	5.8
Ion-exchange resin	0.36	5.8
Nitrohumic acid	1.43	23

* Each powdered sample (100 to 200 mesh) in amount of 1.0 g was immersed in 100 cc of the $CuSO_4 \cdot 5H_2O$ solution containing 2000 ppm of Cu(II) for 24 hours.

** In comparison with that of Xonotlite powders.

Cu(II) with those of the other commercial adsorbent powders (100 to 200 mesh). The amount of each specimen immersed in the solution was 1.0 g. The immersion period was 24 hours. During the immersion the solutions were shaken occasionally. The results indicate that the ability of Xonotlite powders in separating Cu^{2+} ions is much more excellent than those of the other absorbents.

III. 2 Compressive Strength of Xonotlite Compacts in Water

Table IV shows compressive strength in water of the Xonotlite compacts fired at various temperatures for 30 minutes and then immersed in water for one hour. The results on Tobermorite crystal compacts treated under the same condition as described above are also shown in the table. The results indicate that the Xonotlite compacts fired above 200°C have strengths sufficient enough to endure their own loads, even when piled up in water, whereas, Tobermorite compacts all broke down in water.

III. 3 Change in pH of $CuSO_4 \cdot 5H_2O$ solution after immersion of Xonotlite

Figure 2 (a) and (b) show changes in pH of the $CuSO_4 \cdot 5H_2O$ solutions containing 2500 and 200 ppm of Cu(II), respectively, after immersion of the Xonotlite compacts (small cylindrical specimens fired at 600°C for 30 minutes; 3.0 g in total amounts). Figure 3 shows the results of the similar experiments in which water was used in place of the Cu(II) solution. From the figures it can be seen that the values of pH generally

Table IV. Compressive Strengths in Water of Xonotlite and Tobermorite Compacts Fired at Various Temperatures.

Firing temperature (°C)	Xonotlite compacts (Kg/cm²)		Tobermorite compacts
110	break down	(1.2)**	break down in water
200	3.8*	(8.1)**	break down in water
600	11*	(16)**	break down in water
800	11*	(14)**	break down in water
1000	9.5*	(14)**	break down in water

* Strength in water of compacts after immersed in water for one hour.
** Green strength of compacts before immersed in water.

increase with time, go through their maxima, and reach to constant values, respectively. The increase in pH is more rapid for the solution with the low Cu(II) concentration than that of the high concentration. The increase of pH as seen in Fig. 2 and 3 is considered to be caused by dissolution of $Ca(OH)_2$ from Xonotlite into the $CuSO_4 \cdot 5H_2O$ solution; When Xonotlite crystals come in contact with the solution, Ca^{2+} ions at and near the surfaces of the crystals dissolve into the solution and as a result a hydrous SiO_2 layer is formed at the crystal surfaces. When the thickness of this layer reaches to a certain value it usually begins to break down into tiny flakes.[6] The gradual decrease in pH after their maxima as seen in Fig. 2 and 3 would have been caused by dissolution of SiO_3^{-2} from these SiO_2 flakes.

In order to verify the dissolution of the SiO_2 flakes, the following model experiments were made.

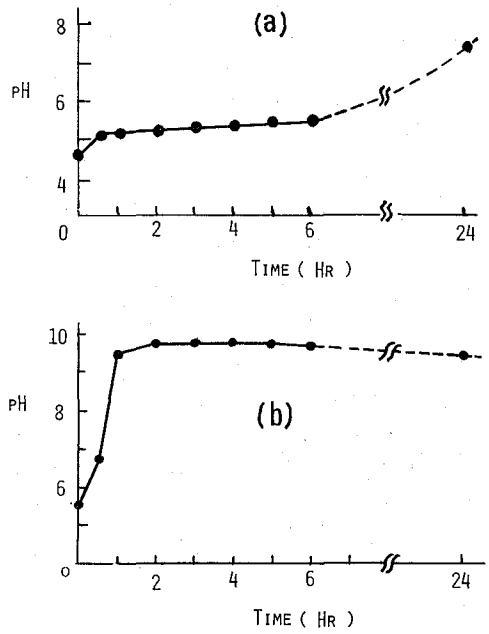

Fig. 2. Changes in pH of $CuSO_4 \cdot 5H_2O$ solutions with time after immersion of Xonotlite compacts. 3.0 gr of Xonotlite compacts fired at 600°C for 30 minutes were immersed in 100 cc of solutions containing 2500 (a) and 200 ppm (b) of Cu(II), respectively.

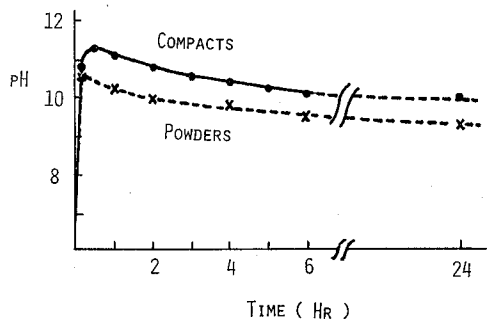

Fig. 3. Change in pH of water with time after immersion of Xonotlite compacts fired at 600°C for 30 minutes. A dotted curve shows results on powdered Xonotlite.

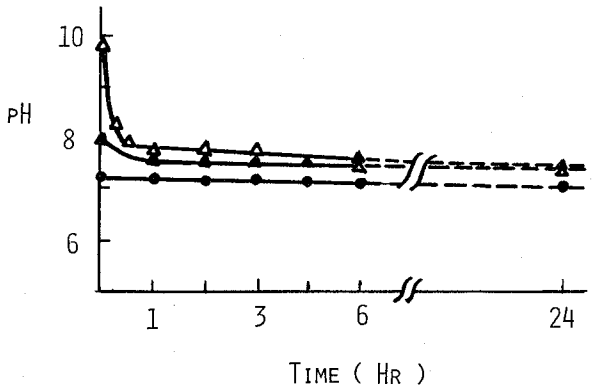

Fig. 4. Changes in pH of mixed solutions of $CuSO_4 \cdot 5H_2O$ and $Ca(OH)_2$ with time after immersion of silica gel. 0.1 g of silica gel was added to 100 cc of each solution.

The pH of the 1% $CuSO_4 \cdot 5H_2O$ solution was changed to 9.8, 8.0, and 7.2, respectively, by adding the appropriate amounts of saturated $Ca(OH)_2$ solution. To 100 cc of each of the solutions thus prepared, 0.1 g of silica gel was added and its change in pH with time was measured. Figure 4 shows the results, which indicate that the silica gel dissolved rapidly into the high alkaline solution, thus lowering its value of pH.

III. 4 **Relation between amount of Cu^{2+} ions Separated and pH of Solution**

The small cylindrical Xonotlite compacts fired at 600°C for 30 minutes were immersed in total amounts of 3.0 g into 100 cc of the $CuSO_4 \cdot 5H_2O$ solution containing 200 ppm of Cu(II). Figure 5 represents the change in amount of the Cu^{2+} ions removed by Xonotlite from the solution with time after immersion of Xonotlite. In the figure the change in pH of the solution is also plotted. It can be seen from the figure that both values increase rapidly after immersion of the Xonotlite compacts, reaching the constant values, respectively, after one hour. The same experiments were made also with the $CuSO_4 \cdot 5H_2O$ solution containing 2500 ppm of Cu(II). The same trend was observed.

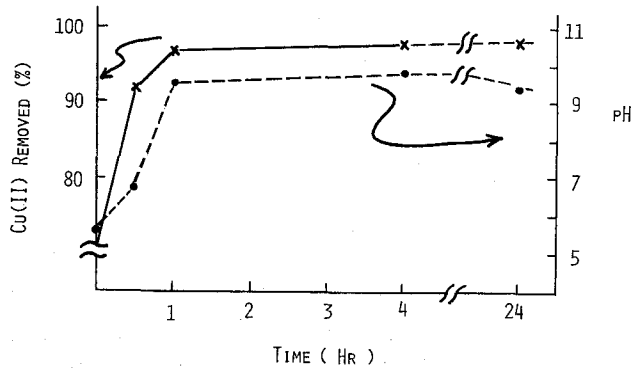

Fig. 5. Changes in amounts of Cu^{2+} ions removed from $CuSO_4 \cdot 5H_2O$ solution with time after immersion of Xonotlite compacts. 3.0 gr of Xonotlite compacts fired at 600°C for 30 minutes were immersed in 100 cc of $CuSO_4 \cdot 5H_2O$ solution containing 200 ppm of Cu(II). A dotted curve shows change in pH of the solution with time.

III. 5 X-ray Diffraction Analyses of Xonotlite Powders before and after their Immersion into $CuSO_4 \cdot 5H_2O$ solution

Figures 6 (a) and (b) show the results of X-ray diffraction analyses of the Xonotlite powders fired at 600°C for 30 minutes and then immersed in 100 cc of the

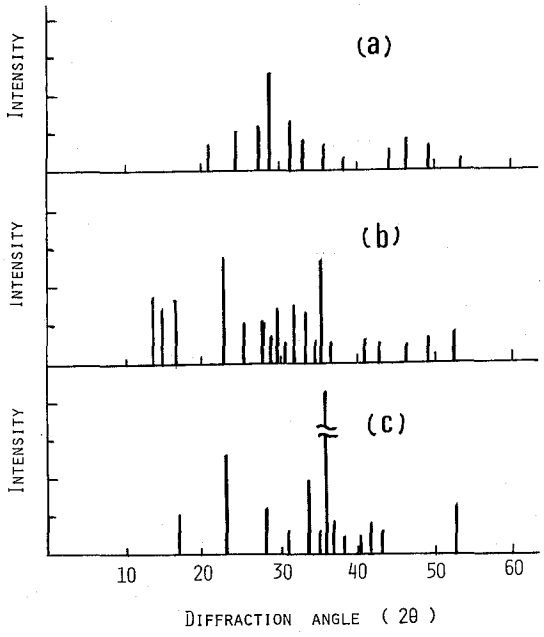

Fig. 6. X-ray diffraction patterns of Xonotlite powders fired at 600°C before and after immersion in $CuSO_4 \cdot 5H_2O$ solution containing 2500 ppm of Cu(II).
(a) Before immersion in $CuSO_4 \cdot 5H_2O$ solution.
(b) After immersed for 24 hours.
(c) Xonotlite compacts after immersed for 24 hours.

$CuSO_4 \cdot 5H_2O$ solution containing 2500 ppm of Cu(II) for 24 hours. In addition to the peaks of the Xonotlite crystals appearing in Fig. 6(a), some other peaks are observed in Fig. 6 (b). In oder to intensify these new peakes, the Xonotlite powders were compressed to form a plate, $20 \times 15 \times 2$ mm, with a pressure of about 10 Kg/cm^2, fired and immersed in the $CuSO_4 \cdot 5H_2O$ solution at the same conditions described above. Figure 6(c) shows an X-ray diffraction pattern obtained by projecting an X-ray beam on the surface of the compressed plate thus prepared. The new peaks were found to corresponds to those characteristic for the basic copper sulphate crystals, $Cu_4SO_4(OH)_6$. This result indicates that the $Cu_4SO_4(OH)_6$ crystals precipitate on the surfaces of the Xonotlite crystals during their immersion in the $CuSO_4 \cdot 5H_2O$ solution.

III. 6 Mechanism of Separation of Ca^{2+} ions from their Solutions by Xonotlite Crystals

From the results of experiments described in III.3, III.4 and III.5, the separation of Ca^{2+} ions from their solutions by Xonotlite crystals is considered to be accompolished by the reactions represented by the following equations:

$$Ca_6Si_6O_{17}(OH)_2 + 6H_2O \longrightarrow H_{12}Si_6O_{17}(OH)_2 + 6Ca(OH)_2 \quad \cdots\cdots(1)$$

$$6Ca(OH)_2 + 8CuSO_4 \longrightarrow 2Cu_4(SO_4)(OH)_6 + 6Ca^{2+} + 6SO_4^{2-} \quad \cdots\cdots(2)$$

(1)+(2)

$$Ca_2Si_6O_{17}(OH)_2 + 8CuSO_4 + 6H_2O \longrightarrow H_{12}Si_6O_{17}(OH)_2 + 2Cu_4(SO_4)(OH)_6 + 6Ca^{2+} + 6SO_4^{2-} \quad \cdots\cdots(3)$$

Namely, when the Xonotlite crystals come in contact with the $CuSO_4 \cdot 5H_2O$ water solution, the Ca^{2+} ions in the Xonotlite crystals dissolve into the solution, increasing the pH of the solution in neighborfood of the Xonotlite crystal surfaces. The increase in pH of the solution causes $Cu_4(SO_4)(OH)_6$ crystals to precipitate at the surfaces of the Xonotlite crystals in which the Ca^{2+} ions have already been exchanged for H^+ ions ($H_{12}Si_6O_{17}(OH)_2$).

Table V shows the results of experiments made for determining a ratio of the equivalent amount of Ca^{2+} ions dissolved from the Xonotlite into the $CuSO_4 \cdot 5H_2O$

Table V. Relation Between Amounts of Ca^{2+} ions Dissolved in $CuSO_4 \cdot 5H_2O$ Solutions and those of Cu^{2+} ions Removed from the Solutions.

Xonotlite powders (g)*	Cu(II) contained in Xonotlite (mg) (theor.)	Ca(II) contained in Xonotlite (equiv.) (theor.)	Ca(II) dissolved (equiv.) (exp.)	Cu(II) removed (equiv.) (exp.)	Ca(II) (exp.)/Ca(II) (theor.)	Cu(II)/Ca(II)
0.03	10.2	0.51	0.43	0.77	0.87	1.79
0.05	17.0	0.85	0.74	1.29	0.87	1.74
0.08	27.2	1.36	1.17	1.78	0.87	1.52
0.10	34.0	1.70	1.34	2.30	0.79	1.71
0.30	102.0	5.10	2.06	3.47**	0.40	1.68
0.50	170.0	8.50	2.04	3.47**	0.24	1.68

* Xonotlite powders (100 to 200 mesh) in various amounts were immersed for 24 hours into 50 cc of the $CuSO_4 \cdot 5H_2O$ solutions containing 2000 ppm of Cu(II).

** Being equal to the amount of Cu^{2+} ion contained in original $CuSO_4 \cdot 5H_2O$ solution.

solution to that of Cu^{2+} ions separated from the solution. According to the equation (3), the above ratio, Cu^{2+}/Ca^{2+}, should be $8/6=1.33$. The values of the ratios given in Table V, which were obtained experimentally, however, were in a range from 1.52 to 1.79, being much larger than 1.33. This discrepancy may be interpreted if one assumes that some parts of the Ca^{2+} and Cu^{2+} ions have been absorbed by the hydrous silica.

IV CONCLUSIONS

1) Xonotlite crystal compacts fired at about 600°C show an excellent ability in separating heavy-metal ions such as Cu^{2+}, Cd^{2+} and Cr^{3+} *etc.* from their solutions.

2) They also show fairly high ability in keeping their shape in the water solution; their compressive strength in water was about 10 Kg/cm^2. The high strength was attributed to entangled fibrous crystal structure of the Xonotlite compacts.

3) The separation of Cu^{2+} ions from their $CuSO_4 \cdot 5H_2O$ solution is caused by dissolution of the Ca^{2+} ions from Xonotlite crystals into the $CuSO_4 \cdot 5H_2O$ solution, which results in precipitation of $Cu_4(SO_4)(OH)_6$ crystals on the surfaces of Xonotlite crystals.

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